



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(54) Title: MACHINE DISHWASHING AND RINSE AID COMPOSITIONS</p> <p>(57) Abstract</p> <p>A machine dishwashing or rinse aid composition having improved performance on glass appearance is disclosed comprising an effective level of a hydrotalcite compound having general empirical formula: <math>[M_{k+m}N_{n+p}(OH)_2]A_z^{y-} \cdot xH_2O</math>, wherein M is any 1+ or 2+ cation or combination thereof; N is any 3+ or 4+ cation or combination thereof; k is the sum of the individual mole fractions of the 1+ cations; m is the sum of the individual mole fractions of the 2+ cations; n is the sum of the individual fractions of the 3+ cations; p is the sum of the individual mole fractions of the 4+ cations; where either but not both of k and m or n and p can be zero and <math>k + m + n + p = 1</math>; <math>A_z^{y-}</math> is any anion of charge y- and mole fraction z, or combination of anions of similar or differing y, and <math>k + 2m + 3n + 4p - 2 - zy + 0</math> and x can range from 1 to 100. Preferred hydrotalcite compounds have the formulas: <math>[Zn_4Al_2(OH)_{12}(NO_3)_2] \cdot xH_2O</math>, and <math>[Mg_4Al_2(OH)_{12}]Cl_2 \cdot 3H_2O</math>.</p>		

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## MACHINE DISHWASHING AND RINSE AID COMPOSITIONS

Field of the invention

This invention relates to machine dish- and warewashing compositions. These compositions are used for the cleaning of housewares such as pots, pans, dishes, cups, saucers, bottles, glassware, crockery, cutlery and other kitchen utensils in automatic-dishwashing and warewashing machines. For brevity sake these compositions are referred to in the description as machine dishwashing compositions.

The invention also relates to rinse aid compositions for use in the final rinse step of the washing machine operation.

15 Background of the invention

Machine dishwashing compositions usually contain as main components a builder or builder mixture, buffering and/or alkaline agents, a bleaching agent which may be a chlorine or oxygen bleach, and lately also enzymes. Such machine dishwashing compositions are used in the main wash step of machine dishwashing and in general have a satisfactory cleaning performance.

It is, however, well known in the dishwashing art that the visual appearance of the cleaned article is a critical factor for a dishwashing composition to be satisfactory to the consumer. Frequently after cleaning of an article a film is formed thereon, which results in the article showing a dull surface when dry, or spots are formed on an article upon drying, both phenomena causing the article to have an "unclean" visual appearance.

It is customary to add to the rinsing water a rinse aid composition which causes the articles to dry more evenly and improves the visual appearance of the articles when dry. Although such rinse aid compositions improve said visual appearance in comparison with articles which have

not been rinsed with a rinse aid containing rinse liquor, said visual appearance may still need improvement, as, despite the use of a rinse aid, some film- and spot-formation may still occur.

5

It is known from EP-A-0,139,329, EP-A-0,139,331 and EP-A-0,140,435 that the incorporation of an effective level of a layered clay in machine dishwashing compositions reduces the problem of film and spot formation on the washed articles, thereby improving the so-called "glass appearance". EP-A-0139.330 discloses the incorporation of a layered clay in a rinse aid composition.

Suitable layered clay minerals according to these art references belong to the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays, which may be either naturally occurring or synthetic, preferably the commercial synthetic hectorites ex Laporte Industries Ltd, known under the tradename Laponite®.

Without wishing to be bound by any theory it is believed that the layered clay performs this task by providing a very large surface area in solution which then picks up food fragments, especially proteins and protein/fat complexes, that would otherwise redeposit onto the washed articles, in other words via the mechanism of adsorption.

Although the glass appearance benefit of Laponite® clay can indeed be demonstrated, the effect is still far from ideal, especially at higher protein concentrations in the wash liquor.

It is therefore that there is a vivid interest amongst researchers to diligently look for better alternatives, since a good glass appearance is one of the most striking effects observed by consumers for judging the quality of a machine dishwashing product.

Object of the invention

It is an object of the invention to provide a machine dishwashing composition having improved performance on glass appearance, i.e. having improved reduction to form films and spots on the articles cleaned therewith. It is another object of the invention to provide an improved rinse aid composition.

Summary of the invention

It has now surprisingly been found that the above object can be achieved by the incorporation in a machine dishwashing composition or in a rinse aid composition of an effective level of a hydrotalcite compound, preferably a Zn/Al or Mg/Al hydrotalcite. The hydrotalcite compound can be used according to the invention as partial or preferably complete replacement for the layered clay of the art.

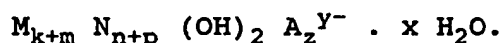
Description of the invention

The term "hydrotalcite" is used herein to refer to the naturally occurring material as well as to the synthetic forms of the hydrotalcite group of compounds. Use of hydrotalcite-like materials as dye-transfer reducing agent in fabric washing detergent compositions is described in EP-A-0,431,867, and use thereof in oral compositions to combat growth of dental plaque is described in EP-A-0,368,420.

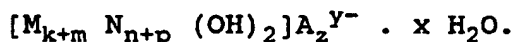
Naturally occurring hydrotalcite is a Mg/Al hydroxy carbonate mineral having a molar composition  $[Mg_6 Al_2(OH)_{16}]CO_3 \cdot 4H_2O$  and consists of positively charged hydroxide sheets alternating with negatively charged inter-layer sheets. The positive charge on the hydroxide sheets arises from isomorphic replacement of approximately one third of magnesium atoms by aluminum creating the necessity for the compound to take up anions in-between the sheets for charge compensation. Thus hydrotalcites are layered compounds with an intracrystalline void space created by

the intercalation of anions and water, which is in contrast to clays that have a negatively charged layer also as a result of isomorphic substitutions and, therefore, intercalate cations for charge balance, making them the charge-wise mirror image of hydrotalcites.

By synthesis, various combinations of mono-divalent (e.g.  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ) and tri-tetravalent cations (e.g.  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Sn}^{4+}$ ) and a wide variety of anions (e.g.  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) are possible giving rise to an entire family of hydrotalcite compounds with the general empirical formula:



The invention therefore provides a machine dishwashing composition or a rinse aid composition comprising an effective level of a hydrotalcite compound having the general empirical formula:



where:

M is any 1 + or 2 + cation or combination thereof;

N is any 3 + or 4 + cation or combination thereof;

k is the sum of the individual mole fractions of the 1 + cations;

m is the sum of the individual mole fractions of the 2 + cations;

n is the sum of the individual mole fractions of the 3 + cations;

p is the sum of the individual mole fractions of the 4 + cations,

where either but not both of k and m or n and p can be zero and  $k + m + n + p = 1$ ;

$\text{A}_z^{y-}$  is any anion of charge  $y^-$  and mole fraction z, or

combination of anions of similar or differing y, and  $k + 2m + 3n + 4p - 2 - zy = 0$  and x can range from 1- 100, depending upon and consistent with the molar composition.

The above definition of the hydrotalcite compound in the composition of the present invention includes the mixed metal hydroxide compounds disclosed by US-A-5,015,409 and US-A-5,154,932, both of which documents are incorporated  
5 herein for all purposes.

Preferred cations M in the above formula are  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ , particularly  $Mg^{2+}$ ,  $Zn^{2+}$  and  $Cu^{2+}$ .

10 Preferred cations N in the above formula are  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Ti^{4+}$ ,  $Sn^{4+}$ , particularly  $Al^{3+}$  and  $Ti^{4+}$ .

The anion A may be inorganic or organic. Preferred inorganic anions A are  $NO_3^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$  and  $Cl^-$ ,  $Br^-$  and  
15  $I^-$ . The best results were achieved with the monovalent anions, such as  $NO_3^-$  and  $Cl^-$ . Examples of organic anions are carboxylate ions, such as citrate and stearate. Preferred compounds are those wherein the M/N ratio does not exceed 5.

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Examples of such hydrotalcite compounds include:

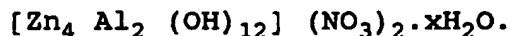
- (i) the natural hydrocalcite,
- (ii) synthetic hydrotalcite,
- (iii) Mg/Al hydroxy nitrates, carbonates, sulphates,  
25 chlorides,
- (iv) Zn/Al hydroxy nitrates, carbonates, sulphates, chlorides,
- (v) Li/Al hydroxy nitrates, carbonates, sulphates, chlorides,
- 30 (vi) Ca/Al hydroxy nitrates, carbonates, sulphates, chlorides,
- (vii) Mg/Fe hydroxynitrates, carbonates, sulphates, chlorides,
- (viii) Zn/Cr hydroxy nitrates, carbonates, sulphates,  
35 chlorides.

Specific examples include:

- 1)  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$
- 2)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 3)  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 5 4)  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot x\text{H}_2\text{O}$
- 5)  $[\text{Mg}_8\text{Al}_2(\text{OH})_{20}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 6)  $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}]\text{CO}_3 \cdot x\text{H}_2\text{O}$
- 7)  $[\text{Zn}_6\text{Al}_2(\text{OH})_{16}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 8)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}](\text{CO}_3) \cdot x\text{H}_2\text{O}$
- 10 9)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\text{SO}_4 \cdot x\text{H}_2\text{O}$
- 10)  $[\text{Li}_2\text{Al}_4(\text{OH})_{12}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 11)  $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 12)  $[\text{Zn}_4\text{Cr}_2(\text{OH})_{12}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- 13)  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}](\text{Cl})_{12} \cdot 3\text{H}_2\text{O}$

15

Though any of the above described hydrotalcite compounds is usable within the invention, preferred hydrotalcites are the Zn/Al and Mg/Al hydroxy nitrates and chlorides. A particularly preferred hydrotalcite is Zn/Al hydroxy  
 20 nitrate of the following molar composition:



wherein x is from 2-5.

The effective level of hydrotalcite compound to be included  
 25 in the machine dishwashing composition of the invention will range from about 0.01 to 40% by weight, usually from 0.1 to 20% by weight, preferably from 0.5 to 10% and most preferably from 0.5 - 5% by weight.

30 Preferably the hydrotalcite material has a particle size of less than 250  $\mu\text{m}$ , more preferably less than 100  $\mu\text{m}$ , i.e. smaller than the micro-filter mesh size of the dishwashing machine. The crystal platelet size of the hydrotalcite material is preferably less than 0.4  $\mu\text{m}$ , more preferably  
 35 less than 0.2  $\mu\text{m}$ , for obtaining a good glass appearance performance.



The machine dishwashing composition of the invention will normally also contain a builder or builder mixture, buffering and/or alkaline agents, optionally but preferably also a bleaching agent and an enzyme or mixtures of  
5 enzymes.

#### The builder material

Builder materials (phosphates and non-phosphate builder materials) are well-known in the art and many types of  
10 organic and inorganic compounds have been described in literature. They are normally used in all sorts of cleaning compositions to provide alkalinity and buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and/or remove alkaline-earth metal ions  
15 from washing solutions.

The builder material usable herein can be any one or mixture of the various phosphate and preferably non-phosphate builder materials, such as for example the  
20 alkalimetal citrates, carbonates and bicarbonates; nitrilotriacetic acid (NTA); dipicolinic acid (DPA); oxydisuccinic acid (ODS); alkyl- and alkenylsuccinates (AKS); layered silicate; and zeolites. They may be present in the composition of the invention in an amount of from  
25 10% up to about 90% by weight, preferably from 20% to 80% by weight.

Particularly preferred builders are citrates, alkenylsuccinates, carbonates, bicarbonates, zeolites, and mixtures thereof.

30

#### The buffering and/or alkaline agent

This is normally an alkalimetal silicate, preferably sodium silicate at a level of from about 1 to about 70% by weight, preferably from 5 to 40% by weight. This material is  
35 employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. Especially effective is sodium silicate having a

mol ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$  of from about 1.0 to about 3.3., preferably from about 1.8 to about 2.5, normally referred to as sodium disilicate.

- 5 NaOH and/or KOH are also commonly used to provide alkalinity in compositions for industrial warewashing machines.

The bleaching agent

- 10 If present the amount of bleaching agent will preferably lie in a range from 1 to 30% by weight. Alkali metal hypochlorite may be incorporated. Other chlorine bleaches are alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids.

15

- Preferred bleaches are the peroxygen bleaches, such as sodium perborate (tetra- or monohydrate) or sodium percarbonate. These are preferably used in conjunction with a bleach activator which allows the liberation of active  
20 oxygen species at a lower temperature. Numerous examples of activators of this type, often also referred to as bleach or peracid precursors, are known in the art. Preferred bleach activators are tetraacetyl ethylene diamine (TAED), glucose pentaacetate (GPA) and the mono-long chain acyl  
25 tetraacetyl glucoses as disclosed in WO 91/10719, but other activators such as choline sulphophenylcarbonate (CSPC) as disclosed in US Patents 4,751,015 and 4,818,426 can be used. The amounts of sodium perborate or percarbonate and bleach activator in the compositions preferably do not  
30 exceed 20% and 10% by weight respectively, e.g. from 4-20% and from 2-10% by weight respectively.

- Another peroxygen bleach is potassium monopersulphate. Further peroxygen bleaches which may be used are the  
35 organic peroxyacids and their metal salts. Typical peroxyacids include:

- (i) peroxybenzoic acid and ring-substituted

peroxybenzoic acids, e.g. peroxy- $\alpha$ -naphthoic acid;  
(ii) aliphatic and substituted aliphatic monoperoxy  
acids, e.g. peroxyauric acid and peroxyauric acid;  
(iii) 1, 12-diperoxydodecanedioic acid (DPDA);  
5 (iv) 1, 9-diperoxyazelaic acid;  
(v) diperoxybrassylic acid; diperoxysebacic acid and  
diperoxyisophthalic acid;  
(vi) 2-decyldiperoxybutane-1,4-dioic acid; and  
(vii) phthaloylamido peroxycaproic acid (PAP)

10

Instead of or together with said bleach activators, a  
bleach catalyst, such as the manganese complexes of EP-A-  
458,397 and the sulphonimines of US Patents 5,041,232 and  
5,047,163 may also be added.

15

#### Enzymes

Amylolytic and/or proteolytic enzymes are normally used.  
The amylolytic enzymes usable herein can be those derived  
from bacteria or fungi. Preferred amylolytic enzymes are  
20 those prepared and described in GB Patent No. 1,296,839,  
  
cultivated from the strains of *Bacillus licheniformis* NCIB  
8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC  
8480 and ATCC 9945 A. Examples of such amylolytic enzymes  
25 are those produced and distributed under the Trade-names of  
SP-95<sup>®</sup> and Termamyl<sup>®</sup> by Novo Industri A/S, Copenhagen,  
Denmark. These amylolytic enzymes are generally presented  
as granules and may have enzyme activities of from about 2  
to 10 Maltose units/milligram. They may be present in the  
30 composition of the invention in amounts such that the final  
composition has amylolytic enzyme activity of from 10<sup>3</sup> to  
10<sup>6</sup> Maltose Units/Kilogram.

The amylolytic activity as referred to herein can be  
35 determined by the method as described by P. Bernfeld in  
"Method of Enzymology" Volume I (1955) page 149.

The proteolytic enzymes usable herein are for example the subtilisins which are obtained from particular strains of B. Subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase<sup>®</sup> supplied by Gist-Brocades  
5 NV, Delft, Holland. and Alcalase<sup>®</sup>, supplied by NOVO Industri A/S Copenhagen, Denmark. Particularly suitable are proteases obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from NOVO Industri A/S under the  
10 Trade names of Esperase<sup>®</sup> and Savinase<sup>®</sup>. The preparation of these and analogues enzymes is described in GB Patent No. 1,243,784. These enzymes are generally presented as granules, e.g. marumes, prills, T-granulates etc., and may have enzyme activities of from 500 to 1700 Glycine  
15 Units/mg. The proteolytic enzyme activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology" Vol. 22 (1938), page 79 (one Anson unit/gram = 733 Glycine Units/milligram).

20 In the compositions of the invention proteolytic enzymes may be present in amounts such that the final composition has proteolytic enzyme activity of from about  $10^6$  to  $10^8$  Glycine Units/Kilogram.

25 Other enzymes, such as lipolytic enzymes may also be incorporated to improve fat removal. Typical examples of commercial lipolytic enzymes are Lipase YL, Amano CE, Wallerstein AW, Lipase My, and Lipolase ex Novo Ind.

30

#### Other optional ingredients

Surfactants though not strictly essential may also be present for detergency, soil removal, foam depression and/or as rinse aids. If present they can be used in an  
35 amount of up to about 60% by weight depending upon their type and properties. Normally in a properly built or highly built composition as is conventional, only small amounts of

low- to non-foaming nonionic surfactant in the order of 0.1-5% by weight are used, preferably from 0.1-4%, to aid detergency and particularly to suppress excessive foaming caused by some protein soil. Higher amounts i.e. 5-60% by weight of highly deterative surfactants, such as the high HLB nonionic surfactants, the anionic sulphate or sulphonate surfactants and the alkyl polyglycoside class of surfactants, may be used in lower builder containing active/enzyme-based compositions. In the context of the present invention a surfactant content from 0 to less than 5% by weight is preferred.

Zinc salts, both soluble and insoluble zinc salts, can also be incorporated as adjuncts for minimizing glass corrosion.

An inert particulate filler especially sodium sulphate may also be incorporated, though in compact powdered composition it should desirably be omitted as practically possible.

The presence of alkali-metal or alkaline earth metal salts of amino polyphosphonic acids such as the sodium or calcium salt of ethylene diamine tetra methylene phosphonic acid, and ethylene hydroxy dimethylene phosphonate may also be preferred because of their stabilizing effect on percompound bleaches and/or their anti-scaling properties. Also polycarboxylate polymeric substances, such as the maleic acid/methacrylic acid copolymers, known under the Trade Name Sokalan CP5<sup>®</sup> may be present to aid in the inhibition of scaling. This latter may be preferred for reasons of non-P containing. Other anti-scaling agents, such as polypeptides may also be used.

The products of the present invention can be manufactured and presented in any physical form such as a powder, liquid, paste or solid blocks or tablets, and are preferably formulated such that they provide a wash liquor

with a pH of between 6 and 13, preferably from 8-11, and more preferably from 9.5-10.5 (measured at a concentration of from 0.1-0.3% by weight in water).

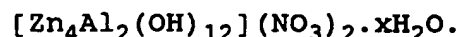
- 5 As explained the invention is also applicable to conventional rinse aid compositions, which usually comprise an aqueous solution comprising a low-foaming nonionic surfactant, citric acid or sodium citrate and optionally a hydrotrope such as a lower alcohol or sodium xylene  
10 sulphonate.

The invention will now be illustrated by way of the following examples (percentages are by weight unless otherwise stated).

15

#### Example I

Preparation of hydrotalcite compound (2)



- 20 94.5 g (1.16 moles) of ZnO were weighed into a 1 litre polypropylene bottle and then slurried in 250 ml of water. 145.1 g (0.39 moles) of  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  were dissolved in 500 ml of water and then added with stirring to the ZnO-slurry.

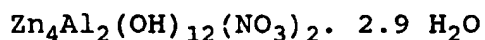
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- The bottle was capped, shaken vigorously and then placed in a thermostatted oven at 90°C for 6 days. The solid was filtered off, washed thoroughly with water and then freeze-dried. The material was finally equilibrated with water  
30 vapour at a water activity of 0.75.

#### Characterization

- Confirmed by XRD to be a layered double hydroxide with a hydrotalcite structure. The basal spacing was 8.8 Å, which  
35 is characteristic of a nitrate form material. The Zn/Al ratio was found by XRF analysis to be 2.0. IR indicated that nitrate was the only anion present. The water content

was determined by thermal analysis and was consistent with the molar composition:



The water was labile and may vary slightly with storage.

5

TEM shows the crystals to be stacks of hexagonal plates of about 0.2  $\mu\text{m}$  diameter. In the solid state these crystal stacks aggregate to form irregular particles of about 20 to 50  $\mu\text{m}$  diameter.

10

#### Example II

The following powdered machine dishwashing composition were prepared:

15	<u>Composition</u>	<u>parts by weight</u>
	Sodium citrate 2 aq.	42
	Sodium disilicate <sup>4)</sup>	35
	Sodium perborate monohydrate	7
	Sokalan CP5 <sup>1)</sup>	5
20	TAED <sup>2)</sup> (83%)	4.2
	Amylase	1.7
	Protease	1.7
	Adsorbing material <sup>3)</sup>	1.7

25 1) = acrylic acid/maleic acid copolymer ex BASF

2) = N, N, N<sup>1</sup>, N<sup>1</sup>-tetraacetylene diamine bleach activator

3) = a) Laponite XLG ex Laporte Industries Ltd

30 b) Synthetic hydrotalcite,  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$

c) Zn/Al hydrotalcite of Example I

d) None

4) = Sodium disilicate containing 20%  $\text{H}_2\text{O}$

35 Machine dishwashing experiments were carried out with the above formulations (a), (b), (c) and (d) at a product dosage of 17 g. per run (= 3.4 g/l) in a Bosch S 510

machine at a water intake of 5 litre (16°FH). The wash programme consisted of a pre-wash, main wash at 55°C, two intermediate rinses and a final rinse of 65°C. Total washing time 65 minutes. The load per wash consisted of a dummy load together with five milk-glasses and two glass-plates. As in glass appearance terms egg yolk is notoriously known as problem-soil, it is used here as the standard-soil. The machine dishwashing product and egg-yolk soiling (a dispersion in ca. 20 ml water) were added to the wash-liquor at the start of the main wash cycle.

A series of five experiments were carried out for each composition with varying egg-yolk concentrations in the wash-liquor i.e.:

- 0.05 g/l
- 0.10 g/l
- 0.20 g/l
- 0.30 g/l
- 0.40 g/l

and the glass-appearance was judged in terms of spot-score according to the following table.

Spot - score	Number of spots
1	none
2	1 - 5
3	6 - 10
4	11 - 20
5	21 - 30
6	31 - 40
7	41 - 50
8	51 - 75
9	76 - 100
10	101 - 150
11	> 150



The results are shown in Figure 1.

It can be seen from this figure that hydrotalcites are superior adjuncts in terms of glass appearance as compared with Laponite clay. Whereas with a composition containing Laponite clay an appreciable number of spots were observed already at an egg-yolk concentration of 0.10 g/l, no spot-formation was observed with the formulations containing hydrotalcites. With composition (b) containing syntehtic hydrotalcite a perceptible spot formation started at egg-yolk concentration of 0.15 g/l, and with composition (c) containing Zn/Al hydrotalcite perceptible spot formation only started at egg-yolk concentration of above 0.30 g/l, which undoubtedly is a significant improvement.

### 15 Example III

In this Example a comparison was made between Laponite clay and Zn/Al hydrotalcite in Machine dishwashing experiments carried out with a similar formulation as used in Example II, but this time the formulation contains a nonionic surfactant.

The same Bosch® S 510 machine, the same wash programme and the same product dosage were used.

	<u>Composition</u>	<u>parts by weight</u>
25	Sodium citrate 2 aq	42
	Sodium disilicate	35
	Sodium perborate monohydrate	7
	Sokalan CP5	5
	TAED (83%)	4.2
30	Amylase	1.7
	Protease	1.7
	Nonionic surfactant	1.7
	Adsorbing material*	1.7

- 35 \* = a) Laponite XLG ex Laporte Industries Ltd  
b) Zn/Al hydrotalcite of Example I.

The soilings used in the experiments were:

- i) egg-yolk
  - ii) ASTM (20% skimmed milk powder + 80% Blue Band margarine)
  - 5   iii) mixture consisting of: 31% mashed potato  
                                          23% pudding  
                                          11% spinach  
                                          15% milk
- 10   In the washing experiments (i) was added in an amount of 0.75 g.; (ii) was added in an amount of 20 g.; and (iii) was added in amounts of 4 g. and 20 g.

15   The results are depicted in Figure 2 which again shows the superiority of the composition of the invention containing Zn/Al hydrotalcite to composition of the art containing Laponite XLG clay.

20   Example IV

          In this Example a comparison was made between various Zn/Al-nitrate hydrotalcites having different platelet crystal sizes, in order to find the effect of the platelet crystal size of chemically different composed hydrotalcites  
25   on the glass appearance improving performance of these hydrotalcites.

          For this purpose, machine dishwashing experiments were carried out with the formulation used in Example II, whereby various types of Zn/Al hydrotalcites having the  
30   chemical formula as shown in Example I and of Mg/Al hydrotalcites having the chemical formula  
           $[Mg_4Al_2(OH)_{12}](NO_3)_2 \cdot xH_2O$  were applied as adsorbing material.

35   The same Bosch® S510 machine, the same wash programme and the same product dosage were used as in Example II.  
          At the start of the main wash cycle, an egg-yolk soiling

(being a dispersion in ca. 20 ml water) was added to the wash liquor, to obtain an egg-yolk concentration in the wash liquor of 0.2 g/litre.

A series of experiments were carried out using the above-mentioned hydrotalcite compounds and the glass appearance was judged in terms of the spot-score according to the table shown in Example II.

The results are depicted in Figure 3 showing the effect of platelet crystal size of the hydrotalcite compounds tested. It can be seen that the best results were achieved with materials having a platelet size less than  $0.4 \mu\text{m}$ . Furthermore, it can be noticed that the chemical composition of the platelets is less important than their size with regard to the glass appearance performance to be obtained.

#### Example V

In this Example, various Zn/Al hydrotalcites having different anions (i.e. nitrate, sulphate and carbonate) were compared, in order to find the influence of the type of anion present in the hydrotalcite applied, on the glass appearance improving performance. Furthermore, the performance of the Zn/Al-nitrate hydrotalcite was compared with that of Mg/Al chloride hydrotalcites.

For this purpose, machine dishwashing experiments were carried out with the formulation used in Example II whereby the following hydrotalcite compounds were applied as adsorbing material:

- (a)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
- (b)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\text{SO}_4 \cdot x\text{H}_2\text{O}$
- (c)  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot x\text{H}_2\text{O}$
- (d) Mg/Al hydrotalcite ex Dow Chemicals, having the chemical composition  $[\text{Mg}_4\text{Al}_4(\text{OH})_{18.65}]\text{Cl}_{1.35} \cdot x\text{H}_2\text{O}$ , wherein the chloride ions and some of the hydroxyl ions are exchangeable and wherein the mixed metal

hydroxide crystals consist of very thin 30-50 nm diameter plates.

- (e)  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ . wherein  $\text{Mg}/\text{Al} \approx 2$  and the mixed metal hydroxide crystals are thin 50 nm diameter hexagonal plates.

The same Bosch® S510 machine, the same wash programme, the same product dosage and the same egg-yolk concentration in the wash liquor were applied as in Example IV.

10

First, a series of experiments were carried out using the above-indicated Zn/Al hydrotalcite compounds (a), (b) and (c), having a platelet size of 0.2  $\mu\text{m}$ , and the glass appearance was judged in terms of the spot score according to the table shown in Example II.

15

The results are depicted in Figure 4 showing the effect of the anion type contained in the Zn/Al hydrotalcite compounds tested. It can be seen that the best glass appearance performance was found when applying the Zn/Al nitrate hydrotalcite.

20

Subsequently, a series of experiments were carried out using the above-indicated Zn/Al nitrate and Mg/Al hydrotalcite compounds (c), (d) and (e), and the glass appearance was once again judged in terms of the spot score according to the table in Example II.

25

In these experiments, the Zn/Al nitrate hydrotalcite consisted of platelets having a size of 0.1  $\mu\text{m}$ .

The results are shown in Figure 5, clearly showing that the Mg/Al chloride hydrotalcite compounds tested delivered performances approaching that of the Zn/Al nitrate hydrotalcite tested.

30

It can also be noticed that a somewhat worse glass appearance performance was found when using Zn/Al nitrate consisting of 0.1  $\mu\text{m}$  platelets than with Zn/Al nitrate having a platelet size of 0.2  $\mu\text{m}$  (see Figure 4). The reason

35

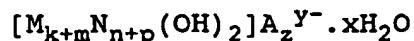
is likely to be a somewhat different egg-yolk composition applied during the two test series. It is noted in this respect that these tests were performed for obtaining relative rather than absolute information about the effect  
5 of the type of anion present in the hydrotalcite.

Miyata [Clays and Clay Minerals 31 (1983) 305] found that hydrotalcites have a lower ion exchange selectivity for monovalent anions such as nitrate, chloride and bromide,  
10 than for divalent anions, such as sulphate and carbonate, and that the monovalent anions can therefore be more readily replaced in ion exchange reactions.

Taking this into account, it can be concluded from the results shown in Figures 4 and 5 that the ability of the  
15 hydrotalcites of the present invention to readily undergo ion exchange is beneficial for the glass appearance performance and that hydrotalcites with monovalent anions, such as nitrate and chloride, are preferred compounds in this respect.

## CLAIMS

1. A machine dishwashing composition comprising a builder or builder mixture, buffering and/or alkaline agent, characterized in that it further comprises an effective level of a hydrotalcite compound having the general empirical formula:



where

M is any 1 + or 2 + cation or combination thereof;

N is any 3 + or 4 + cation or combination thereof;

k is the sum of the individual mole fractions of the 1 + cations;

m is the sum of the individual mole fractions of the 2 + cations

n is the sum of the individual fractions of the 3 + cations;

p is the sum of the individual mole fractions of the 4+ cations, where either but not both of k and m or n and p can be zero and  $k + m + n + p = 1$ ;

$A_z^{y-}$  is any anion of charge  $y^-$  and mole fraction  $z$ , or combination of anions of similar or differing  $y$ , and  $k + 2m + 3n + 4p - 2 - zy = 0$  and  $x$  can range from 1 to 100.

2. A composition according to claim 1, characterized in that said hydrotalcite compound is used as adjunct for improving glass appearance.
3. A composition according to claim 1 or 2, characterized in that M is selected from  $Mg^{2+}$ ,  $Zn^{2+}$  and  $Cu^{2+}$  and mixtures thereof; N is selected from  $Al^{3+}$  and  $Ti^{4+}$  and mixtures thereof; and  $A^{y-}$  is selected from  $CO_3^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$  and  $SO_4^{2-}$ .

4. A composition according to claim 3, characterised in that M is selected from  $Mg^{2+}$ ,  $Zn^{2+}$  and mixtures thereof; N is  $Al^{3+}$ ; and  $A^{Y-}$  is selected from  $NO_3^-$  and  $Cl^-$ .
5. A composition according to claim 1, 2 or 3, characterized in that it comprises from 0.01 to 40% by weight of said hydrotalcite compound.
6. A composition according to claim 1, 2, 3 or 4, characterized in that the hydrotalcite compound is selected from the group of compounds having the formula:
  - (a)  $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$
  - (b)  $[Mg_4Al_2(OH)_{12}]Cl_2 \cdot 3H_2O$ ;
  - (c)  $[Zn_4Al_2(OH)_{12}](NO_3)_2 \cdot xH_2O$ ; and
  - (d)  $[Mg_4Al_4(OH)_{18.65}]Cl_{1.35} \cdot xH_2O$  ,wherein x is from 2-5.
7. A composition according to any of the preceding claims 1-6, characterized in that it further comprises a bleaching agent.
8. A composition according to any of the preceding claims 1-7, characterized in that it further comprises from 0.1 to 5% by weight of a nonionic surfactant.
9. A composition according to any of the preceding claims 1-7, characterized in that it further comprises an enzyme.
10. A composition according to claim 9, characterized in that said enzyme is an amylolytic enzyme.
11. A composition according to claim 9, characterized in that said enzyme is a proteolytic enzyme.

12. A rinse aid composition suitable for use in an aqueous rinse liquor, characterized in that it comprises a hydrotalcite compound as defined in claims 1-6.



Fig.1.

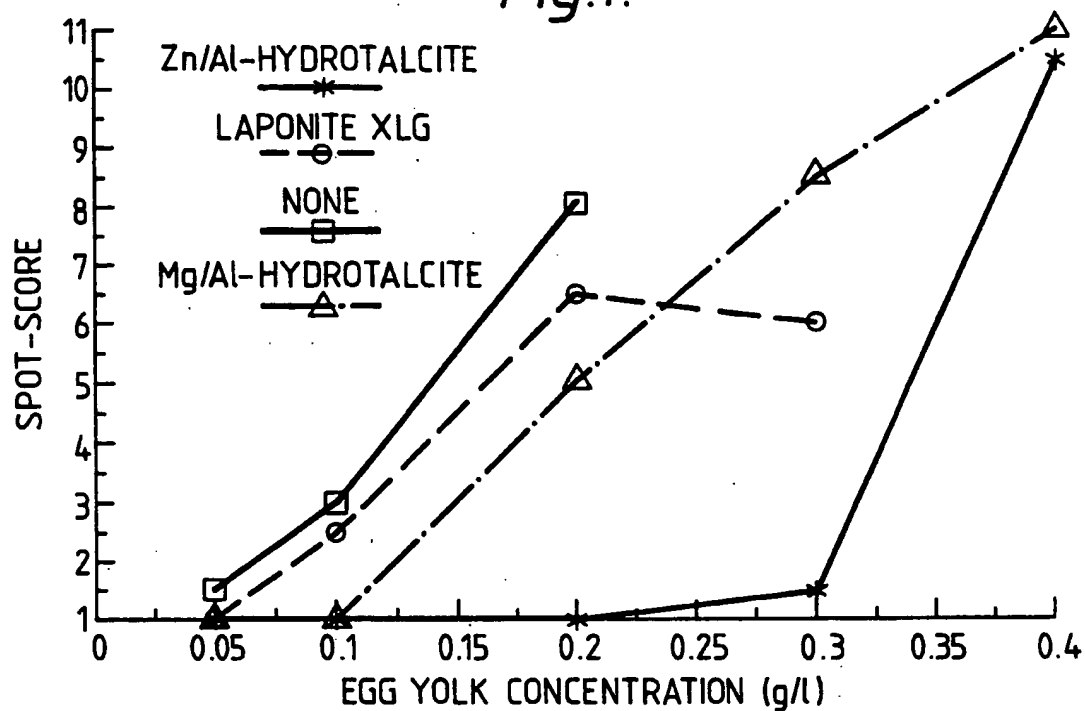


Fig.2.

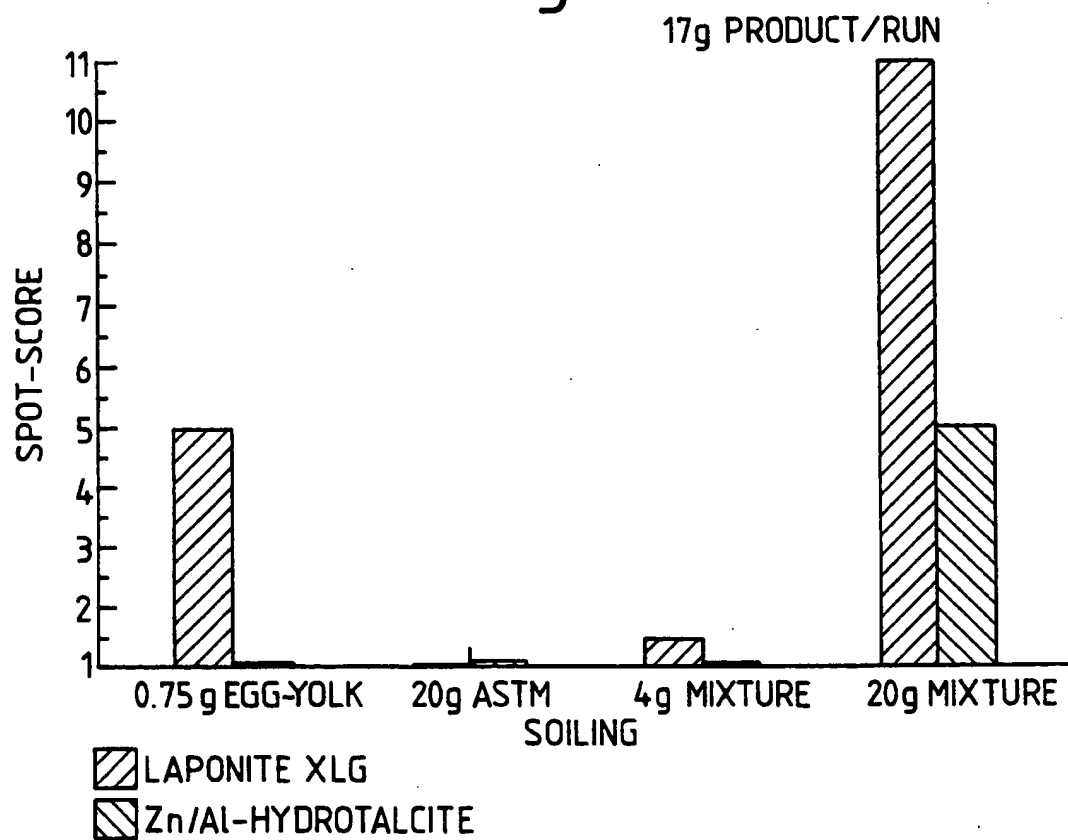


Fig.3.

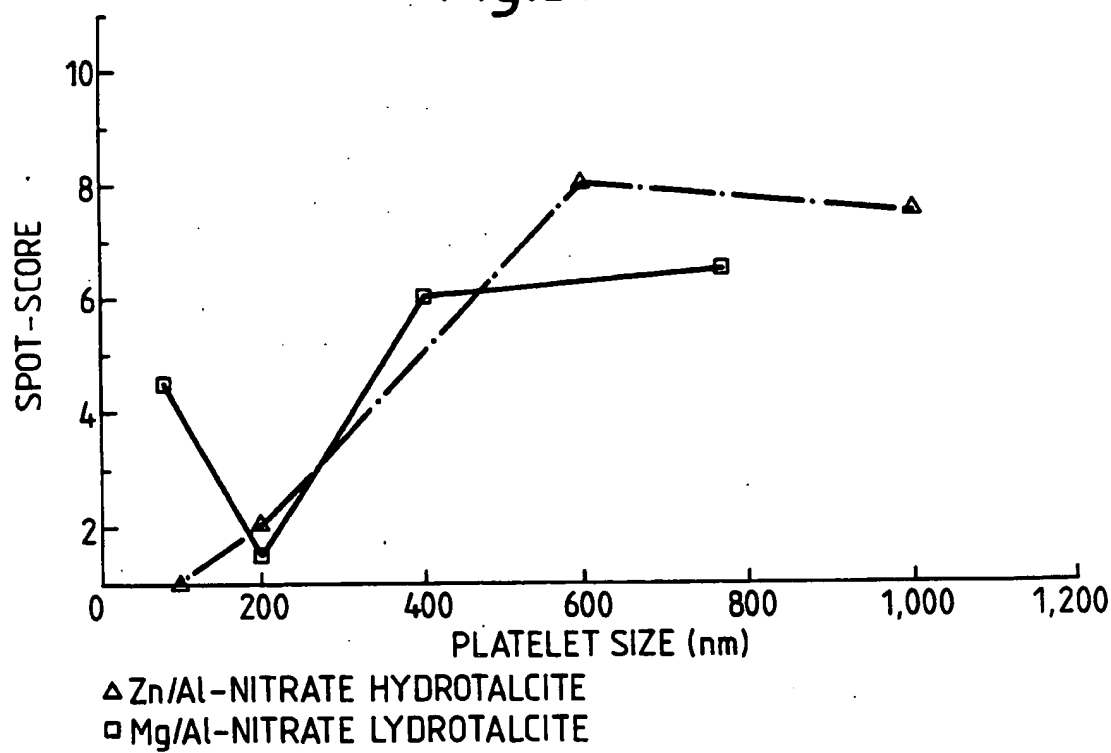
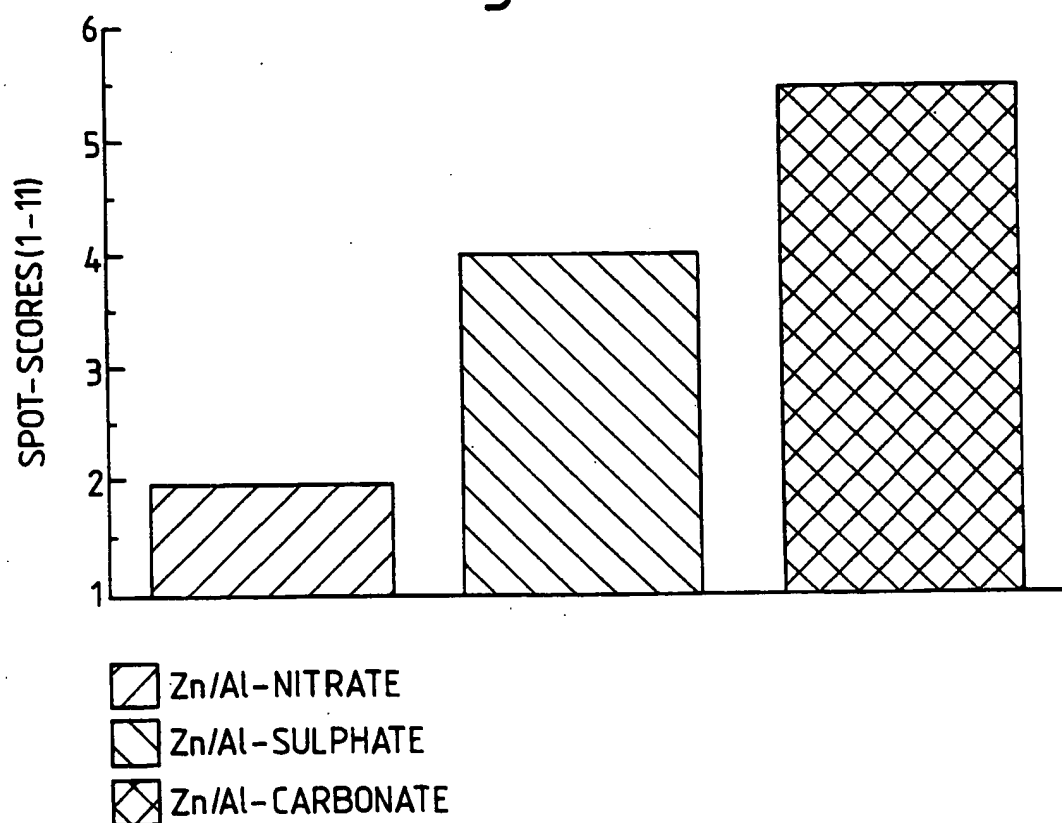
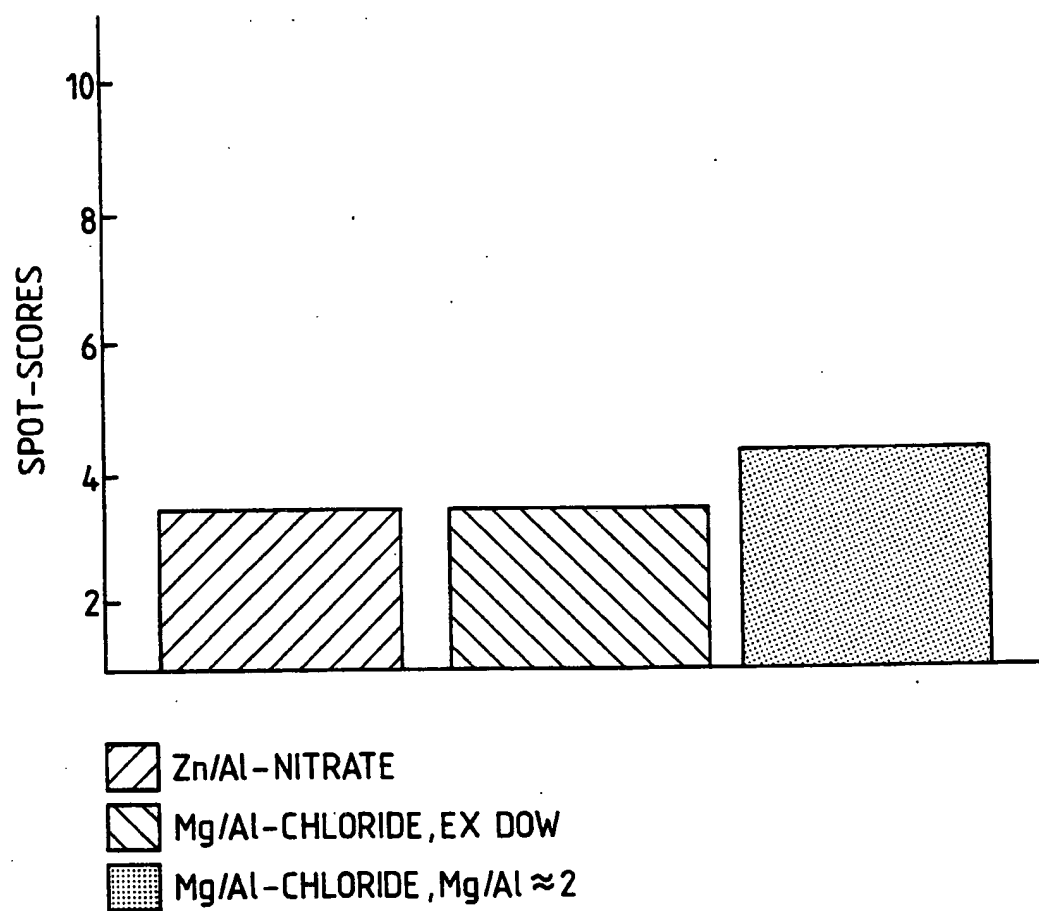


Fig.4.



*Fig. 5.*

## INTERNATIONAL SEARCH REPORT

PCT/EP 93/01996

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C11D3/12		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C11D ; C01F ; C01G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	WO,A,8 908 693 (THE DOW CHEMICAL CO) 21 September 1989 see page 6, last paragraph see page 7, line 1 - line 12 see page 9, line 21 - line 29 see page 12; example 5 see claims 1-10	1,3-5,7
A	EP,A,0 345 587 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 13 December 1989 see the whole document	1,3-11
A	EP,A,0 369 275 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 23 May 1990 see page 3, line 50 - line 58	1
		-/--
<sup>10</sup> Special categories of cited documents : <sup>"A"</sup> document defining the general state of the art which is not considered to be of particular relevance <sup>"E"</sup> earlier document but published on or after the international filing date <sup>"L"</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) <sup>"O"</sup> document referring to an oral disclosure, use, exhibition or other means <sup>"P"</sup> document published prior to the international filing date but later than the priority date claimed <sup>"T"</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention <sup>"X"</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step <sup>"Y"</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. <sup>"A"</sup> document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search  02 DECEMBER 1993		Date of Mailing of this International Search Report  22. 12. 93
International Searching Authority  EUROPEAN PATENT OFFICE		Signature of Authorized Officer  SIATOU E.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 063 631 (KYOWA CHEMICAL INDUSTRY CO LTD) 3 November 1982 see claims 1-7 ---	1
A	EP,A,0 431 867 (UNILEVER PLC ET AL) 12 June 1991 cited in the application see the whole document -----	1-6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9301996  
SA 77613

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO-A-8908693	21-09-89	US-A-	5015409	14-05-91
		EP-A-	0364543	25-04-90
		JP-T-	2503688	01-11-90
		US-A-	5232627	03-08-93
-----				
EP-A-0345587	13-12-89	DE-A-	3819191	07-12-89
		WO-A-	8912088	14-12-89
		EP-A-	0422020	17-04-91
		JP-T-	3504869	24-10-91
		US-A-	5145599	08-09-92
-----				
EP-A-0369275	23-05-90	DE-A-	3838532	17-05-90
		AU-B-	627806	03-09-92
		AU-A-	4634489	12-06-90
		WO-A-	9005706	31-05-90
		EP-A-	0442951	28-08-91
		JP-T-	4501529	19-03-92
-----				
EP-A-0063631	03-11-82	None		
-----				
EP-A-0431867	12-06-91	AU-B-	634000	11-02-93
		AU-A-	6767990	06-06-91
		JP-A-	4159400	02-06-92
		US-A-	5149456	22-09-92
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